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Asynchronous reductive release of iron and organic carbon from hematite–humic acid complexes

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ABSTRACT

Solid-phase iron (Fe) plays an important role in the accumulation and stabilization of soil organic matter (SOM). However, ferric minerals are subject to redox reactions, which can compromise the stability of Fe-bound SOM. To date, there is limited information available concerning the fate of Fe-bound SOM during redox reactions at Fe mineral surfaces. In this study, we investigated the release kinetics of hematite-bound organic carbon (OC) during the abiotic reduction of hematite–humic acid (HA) complexes by dithionite, to elucidate important processes governing the stability and fate of organic matter during the redox processes. Our results indicate that the reductive release of Fe obeyed first-order kinetics with release rate constants of $6.67–13.0 \times 10^{-3}$ min^{-1}. The Fe-bound OC was released rapidly during the initial stage with release rate constants of 0.011–1.49 min^{-1}, and then became stable with residual fractions of 4.6–58.2% between 120 and 240 min. The release rate of aromatic OC was much faster than for the non-aromatic fraction of HA, and 90% of aromatic OC was released within the first hour for most samples. Our findings show that in the reductive reaction the mobilization of Fe-bound OC was asynchronous with the reduction of Fe, and aromatic OC was released more readily than other components of SOM. This study highlights the importance of evaluating the release of SOM bound with Fe during the redox reactions, especially the influence of the physicochemical properties of SOM.

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1. Introduction

Soil organic matter (SOM) contains 1500 gigatons (Gt) of carbon, approximately double the amount of carbon present in the atmosphere and triple that in terrestrial vegetation (Amundson, 2001; Houghton, 2007; Lal, 2004). A significant amount of carbon (~3.5 Gt per year) is released from soil to the atmosphere as a result of SOM decomposition, contributing to an increase in the concentration of greenhouse gases (Houghton, 2007). Conversely, if effective soil management practices are implemented, SOM can act as a sink for atmospheric carbon, and help mitigate the harmful effects of global warming (Houghton, 2007; Kaiser and Guggenberger, 2003). The soil carbon reservoir can be beneficial as a carbon sink only if SOM is stabilized and stored for relatively long periods. Understanding the stabilization of SOM is important for not only evaluating and predicting the biogeochemical cycles of carbon, but also for effectively managing soil ecosystems under global climate change.

Iron (Fe) oxides have been suggested as important mineral phases for stabilizing SOM, as SOM can be sorbed onto Fe oxides with high sorption affinity (Kaiser and Guggenberger, 2000; Kaiser and Zech, 2000; Lalonde et al., 2012). The sorption capacity for organic matter onto Fe oxide is 110–140 mg C/g, approximately ten times the value of aluminum oxides (Kaiser and Guggenberger, 2007; Tipping, 1981). As a result, over 20% of SOM in soil can be bound to Fe oxides (Wagai and Mayer, 2007). The sorptive association with minerals can protect SOM from degradation by physicochemical sequestration, thereby enhancing SOM stability (Torn et al., 1997; Zimmerman et al., 2002). Hence, understanding the fate of Fe-bound SOM is critical for evaluating the stability of SOM.

Fe(III) oxides are subject to redox reactions, which can break down Fe(III) oxide–SOM complexes and compromise the stability of Fe-bound SOM. Redox reactions of Fe(III)/Fe(II) can be mediated by various abiotic and biotic agents in the soil environment, under the anaerobic–aerobic transitions which occur in natural soils (Chacon et al., 2006; Lipson et al., 2010; Rivkina et al., 1998). Many metal-respiring bacteria derive energy from the reduction of Fe(III) for cell growth and microbial activities (Brock and Gustafson, 1976; Lovley, 1997; Lovley and Phillips, 1986, 1988). Previous geobiological studies have documented the importance of SOM in Fe redox reactions, where it may act as an electron shuttle, electron donor or electron acceptor (Kappler et al., 2004; Lovley, 1997; Lovley et al., 1996; Lovley and Phillips, 1986; Roden

et al., 2010; Scott et al., 1998). Although recent studies have shown that the redox reactions of Fe(III) oxide can be important for the mobilization and degradation of SOM (Grybos et al., 2007, 2009; Hall and Silver, 2013), there is limited information available concerning how Fe-bound organic matter is released and metabolized during redox reactions.

In this study, we investigated the release of hematite-bound organic matter during the reduction of Fe(III) by sodium dithionite, to elaborate the important processes for organic carbon (OC) during the redox reactions. Dithionite is one of the most commonly used Fe(III)-reducing agents for abiotic Fe reduction experiments (Eusterhues et al., 2014; Poulton and Canfield, 2005). We used a relatively low dithionite concentration to slow down the reduction kinetics and simulate natural environmental conditions. Using this abiotic reducing agent is very valuable and helpful for illustrating the governing processes for OC stability during the reduction dissolution of ferric Fe. The impact of the molecular structure of Fe-bound organic matter on the reductive release of OC was also analyzed.

2. Materials and methods

2.1. Materials

Hematite was purchased from Fisher Chemical (Fisher Scientific, Pittsburgh, PA, USA) and used as received. The mineral phase was confirmed by X-ray diffraction (XRD) analysis. The surface area, determined by an AutoChem II 2920 (Micromeritics, Norcross, GA, USA), was 1.9 m^2/g. Model SOM with a wide range of chemical compositions was generated using three sequential extractions of humic acids (HAs) from a peat soil (Supplementary material, Table S1). Detailed information for extraction and characterization of the HAs is available in previous publications (Yang et al., 2011, 2012, 2013). Because the HAs were sequentially extracted from the same peat soil, this minimized the influence of other geochemical factors that might arise if using organic matter from different sources, such as different geological parent materials (Yang et al., 2011, 2012, 2013). Application of these previously extensively characterized HAs with a range of chemical composition provided us with an opportunity to study the role of different functional groups in the release and fate of OC during redox reactions. Specifically, quinones are thought to be important functional groups involved in the redox process (Lovley et al., 1996; Scott et al., 1998). There is a large variation in the content of quinone functional groups in the humic substances we used, which is beneficial for studying the role of quinones in the redox reactions of Fe and consequent processes for Fe-bound OC. For this study, the three HAs (HA1, HA2, and HA3) were dissolved in 0.5 M NaOH solution overnight and centrifuged at 3000 rpm to produce stock solutions with a concentration of 100 mg OC/L, as described in Adhikari and Yang (2015). All other chemicals used in this study were above analytical grade.

2.2. Synthesis of hematite–HA complexes and characterization for complexes

Hematite–HA complexes were made by sorbing HAs onto hematite under a range of pH values. Hematite and HA solution were mixed with a mass/volume ratio of 4 g/120 mL and shaken for 24 h to reach equilibrium. The mixtures were centrifuged at 10,000 rpm for 10 min and the hematite–HA complexes were collected and dried in an oven at 49 °C for 40 h. Hematite–HA complexes were made at pH 5, 7 and 9, by adjusting with HCl or NaOH, to represent the wide range of pH values present in natural soils (Sparks, 2003). The pH influences the conformation of HA; when the pH is relatively low, more aggregate structures form. Hematite–HA complexes synthesized at different pH also can provide insights into the role of SOM conformation during redox reactions, which may influence the degradation and fate of the

SOM. In total, nine different hematite–HA complexes were made in this study (i.e. three different HAs, each at pH 5, 7 and 9).

2.3. Dithionite reduction

Reduction of hematite was performed using the sodium bicarbonate, tri-sodium citrate and sodium dithionite (BCD) method (Holmgren, 1967). The reduction experiments were performed in duplicate. An aliquot (0.2 g) of dried hematite–HA complex was mixed with 15 mL buffer solution (pH 5) containing 1 M $NaHCO_3$, 0.3 M $Na_3C_6H_5O_7$ and 0.15 M $Na_2S_2O_4$. The mixtures were shaken at 100 rpm. At intervals over 960 min, samples were centrifuged at 10,000 rpm for 10 min and the supernatants were removed. The residue was rinsed with 15 mL of distilled, deionized water and centrifuged again. Rinse water was combined with previously collected supernatant for analysis of aqueous Fe. The residues were dried in an oven at 49 °C until the weight was stable (change in weight <0.1%) and then used for residual carbon concentration analysis with an elemental analyzer (EuroVector SpA, Milan, Italy). Pure hematite was used as a control to quantify the reduction of Fe(III) by the BCD method. To analyze the non-reductive release of Fe-bound OC, hematite–HA complexes were reacted with a solution containing 1 M $NaHCO_3$ and 2.25 M NaCl (for equivalent ionic strength), following the same procedure for the reduction reaction. The release of carbon and Fe were analyzed. The influence of citrate sorption on the analysis of residual OC was tested by mixing pure hematite with 0.3 M $Na_3C_6H_5O_7$, 1 M $NaHCO_3$ and 0.45 M NaCl at pH 5, and hematite was collected at different times to analyze OC concentration.

2.4. Release kinetics of Fe and carbon

The release kinetics of Fe were obtained in two ways. Firstly, as sorbed organic matter contributes less than 1% of the total mass of the complexes, the mass of particles at different intervals was used to calculate the residual fraction of Fe. Secondly, the solution-phase Fe was analyzed using inductively coupled plasma with atomic emission spectroscopy (ICP-AES: Varian-Vista AX CCD, Palo Alto, CA, USA) by measuring the optical absorption of Fe at 259.9 nm. The reductive release kinetics of hematite-bound OC was measured simultaneously by analyzing the carbon concentration of the solid residue using an elemental analyzer (EuroVector SpA, Milan, Italy). We corrected the residual carbon fraction analyses by subtracting the sorption of citrate on hematite (2 mg OC/g hematite), determined in the control experiment (Supplementary material, Fig. S1). The residual amount of carbon was calculated based on the carbon concentration and mass of particles collected after each period of reduction. These analyses were only possible for samples within 240 min of reaction, after which residual particles were too low in abundance to be accurately measured.

2.5. Release kinetics of aromatic carbon

Release kinetics for aromatic carbon were measured using a precipitation/re-dissolution method. To precipitate the HA released during the Fe reduction process, the pH of the supernatant collected from the reduction release experiments was reduced to below 1 by adding concentrated HCl. The HAs in the low-pH supernatant were then allowed to precipitate for 1 h and then centrifuged at 3000 rpm for 10 min. The supernatant was discarded and the precipitated HA was rinsed with 10 mL of 1 M HCl to remove any residual Fe. The harvested HA was then re-dissolved in 8 mL of 1 M NaOH. The amount of aqueous aromatic OC was quantified by measuring the UV absorbance at 254 nm (UV_{254}) (Weishaar et al., 2003).

2.6. Carbon 1s near-edge X-ray absorption fine structure

Carbon 1s near-edge X-ray absorption fine structure (NEXAFS) analysis was performed for selected samples, i.e. original HA1, HA1–